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RESEARCH MEMORANDUM

THEORETICAL MAXIMUM PERFORMANCE OF LIQUID FLUORINE - LIQUID OXYGEN MIXTURES WITH JP-4 FUEL AS ROCKET PROPELLANTS

By Sanford Gordon and Roger L. Wilkins

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Cleveland, Ohio

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THEORETICAL MAXIMUM PERFORMANCE OF LIQUID FLUORINE - LIQUID OXYGEN MIXTURES WITH JP-4 FUEL AS ROCKET PROPELLANTS

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SUMMARY

Theoretical values of rocket performance parameters were calculated for JP-4 fuel and various mixtures of liquid fluorine and liquid oxygen, assuming both equilibrium and frozen composition during the expansion process. Data were calculated at several equivalence ratios for each assigned fluorine-oxygen mixture.

The parameters included were specific impulse, combustion-chamber temperature, nozzle-exit temperature, equilibrium composition, mean molecular weight, characteristic velocity, coefficient of thrust, and ratio of nozzle-exit area to throat area.

The maximum value of specific impulse for a chamber pressure of 300 pounds per square inch absolute and an exit pressure of 1 atmosphere (expansion ratio, 20.41) is 299.4 pound-seconds per pound for equilibrium composition and 278.9 pound-seconds per pound for frozen composition. These values occur at 69.75 weight percent fluorine in the oxidant and 20.90 weight percent fuel in the propellant.

INTRODUCTION

Considerable interest has been shown recently in the use of mixtures of liquid fluorine and liquid oxygen as oxidants with hydrocarbons as fuel for possible high-energy rocket propellants (refs. 1 to 3). Mixtures of fluorine and oxygen exist that give higher performance with hydrocarbons than either 100-percent oxygen or fluorine because the fluorine burns preferentially with the hydrogen and the oxygen with the carbon.

Theoretical performance calculations of a typical JP-4 fuel with various mixtures of fluorine and oxygen were made at the NACA Lewis laboratory, (1) to provide data in support of an experimental program, (2) to determine the maximum performance for any assigned fluorine-oxygen mixture as a function of equivalence ratio, and (3) to determine the maximum performance of the propellant as a function of both fluorine-oxygen mixture and equivalence ratio.

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The data were calculated on the basis of both equilibrium and frozen composition during expansion. The performance parameters included are specific impulse, combustion-chamber temperature, nozzle-exit temperature, equilibrium composition, mean molecular weight, characteristic velocity, coefficient of thrust, and ratio of nozzle-exit area to throat area.

SYMBOLS

The following symbols are used in this report: 3473

A nozzle area, sq ft

a local velocity of sound, ft/sec

C_F coefficient of thrust, Ig/c^*

c^* characteristic velocity, gP_cA_t/w, ft/sec

g acceleration due to gravity, 32.174 ft/sec^2

H_T^o sum of sensible enthalpy and chemical energy, cal/mole

h sum of sensible enthalpy and chemical energy per unit weight,

$$\frac{\sum_i n_i(H_T^o)_i}{nM}, \text{ cal/g}$$

I specific impulse, lb-sec/lb

M molecular weight

n number of moles

P pressure

r equivalence ratio, ratio of four times the number of carbon atoms plus the number of hydrogen atoms to twice the number of oxygen atoms plus the number of fluorine atoms

T temperature, ^oK

w rate of flow, lb/sec

α ratio of equivalent oxidant formulas OF_β to equivalent fuel formulas CH_γ

Subscripts:

c combustion chamber

e nozzle exit

i product of combustion

t nozzle throat

β fluorine-to-oxygen atom ratio

γ hydrogen-to-carbon atom ratio

CALCULATION OF PERFORMANCE DATA

The computations were carried out by means of the method described in reference 4 with modifications to adapt it for use with an IBM Card-Programmed Electronic Calculator. The machine was operated with floating decimal point notation and eight significant figures. The successive approximation process which was used to calculate the desired values of the assigned parameters (mass balance and pressure or entropy balance) was continued until seven-figure accuracy was reached.

Assumptions. - The calculations were based on the following usual assumptions: perfect gas law, adiabatic combustion at constant pressure, isentropic expansion, no friction, homogeneous mixing, and one-dimensional flow. The products of combustion were assumed to be graphite and the following ideal gases: atomic carbon C, carbon monofluoride CF, carbon difluoride CF_2, carbon trifluoride CF_3, carbon tetrafluoride CF_4, difluoroacetylene C_2F_2, methane CH_4, carbon monoxide CO, carbon dioxide CO_2, atomic fluorine F, fluorine F_2, atomic hydrogen H, hydrogen H_2, hydrogen fluoride HF, water H_2O, atomic oxygen O, oxygen O_2, and hydroxyl radical OH.

Thermodynamic data. - The thermodynamic data for all combustion products except graphite, methane, the fluorocarbons, and water were taken from reference 4. Data for graphite were taken from reference 5, carbon monofluoride from reference 6, the remainder of the fluorocarbons from reference 7, and water from reference 8. Data for methane were determined by the rigid-rotator-harmonic-oscillator approximation using spectroscopic data taken from reference 9.

The dissocation energy of F_2 was taken to be 35.6 kilocalories per mole and the heat of sublimation of graphite at 298.16° K was taken to be 171.698 kilocalories per mole (ref. 10).

Physical and thermochemical data. - The JP-4 fuel used in these calculations was assumed to have a hydrogen-to-carbon weight ratio of 0.163 (atom ratio $\gamma = 1.942$) and a lower heat of combustion value of 18,640 Btu per pound. Additional properties of jet fuels may be found in reference 11. Several properties of the oxidants taken from references 4, 10, 12, and 13 are listed in table I.

Formulas. - The formulas used in computing the various parameters are as follows:

Specific impulse, lb-sec/lb 3473

$$I = 294.98\sqrt{\frac{h_c - h_e}{1000}} \tag{1}$$

Throat area per unit flow rate, (sq ft)(sec)/lb (pressure in atm)

$$\frac{A_t}{w} = \frac{1.3144T_t}{P_t M_t a} \tag{2}$$

Characteristic velocity, ft/sec

$$c^* = \frac{gP_cA_t}{w} = \frac{32.174P_cA_t}{w} \tag{3}$$

Coefficient of thrust

$$C_F = \frac{Ig}{c^*} = \frac{32.174I}{c^*} \tag{4}$$

Nozzle-exit area per unit flow rate, (sq ft)(sec)/lb (pressure in atm)

$$\frac{A_e}{w} = \frac{0.040853T_e}{P_e M_e I} \tag{5}$$

Ratio of nozzle-exit area to throat area

$$\frac{A_e}{A_t} = \frac{A_e/w}{A_t/w} \tag{6}$$

THEORETICAL PERFORMANCE DATA

The calculated values of performance parameters were obtained for 12 fluorine-oxygen ratios for a combustion pressure of 300 pounds per

square inch absolute and an exit pressure of 1 atmosphere. For each assigned fluorine-oxygen mixture, the following scheme was used to calculate an equivalence ratio for which specific impulse is near maximum:

Let the equivalent formula of the propellant be

$$CH_\gamma + \alpha(OF_\beta)$$

3473

Then by definition the equivalence ratio becomes

$$r = \frac{4 + \gamma}{\alpha(2 + \beta)}$$

For $\beta \leq \gamma$ and assuming products to be CO, HF, and H_2O,

$$\alpha = \frac{2 + \gamma}{2 + \beta} \quad \text{and} \quad r = \frac{4 + \gamma}{2 + \gamma} \tag{7}$$

For $\beta > \gamma$ and assuming products to be graphite, CO, and HF,

$$\alpha = \frac{\gamma}{\beta} \quad \text{and} \quad r = \frac{\beta(4 + \gamma)}{\gamma(2 + \beta)} \tag{8}$$

The simplified set of combustion products was used only to estimate the equivalence ratio giving near maximum specific impulse, whereas the actual calculations included all the combustion products considered in this report. For each of the 12 fluorine-oxygen mixtures, performance data were obtained for three equivalence ratios, including the one given by equation (7) or (8). The calculated values of specific impulse, with both equilibrium and frozen composition assumed during expansion, are given in table II. The values of the other performance parameters and the composition of the combustion products (corresponding to the eqivalence ratios for which equilibrium specific impulse is maximum) are given in tables III and IV for each of the 12 fluorine-oxygen mixtures. The mole fractions of CF_4, CH_4, and F_2 were omitted from table IV inasmuch as they were always less than 0.00001.

Parameters. - The parameters are plotted in figures 1 to 5. Figure 1 indicates the variation of specific impulse with weight percent fluorine in the oxidant for both equilibrium and frozen composition during the expansion process at the equivalence ratio for which equilibrium specific impulse is maximum. The maximum value of specific impulse is 299.4 pound-seconds per pound for equilibrium composition and 278.9 pound-seconds per pound for frozen composition. These maximum values occur at 69.75 weight percent fluorine in the oxidant and 20.90 weight percent fuel in the propellant. The oxidant mixture has the same fluorine-to-oxygen atom ratio as the hydrogen-to-carbon atom

ratio in the fuel (1.942). For this oxidant mixture, the 20.90 weight percent fuel in the propellant is the one in which the number of H atoms equals the number of F atoms and the number of C atoms equals the number of O atoms. These atom ratios may be represented by the equivalent formula $CH_{1.942} + OF_{1.942}$. This formula is consistent with the assumption that hydrogen burns preferentially with fluorine and carbon with oxygen.

A comparison of the maximum values of specific impulse for JP-4
fuel with 69.75 weight percent fluorine in the oxidant, 100 percent 3473
fluorine, and 100 percent oxygen is shown in the following table:

Composition	69.75 percent F_2 30.25 percent O_2 by weight	Fluorine		Oxygen	
	Specific impulse, I	Specific impulse, I	Decrease, percent	Specific impulse, I	Decrease, percent
Equilibrium	299.4	278.9	7.4	260.7	14.8
Frozen	278.9	264.6	5.4	250.4	11.4

The curves of c^*, C_F, T_c, T_e, M_c, M_e, and A_e/A_t against weight percent fluorine in the oxidant, given in figures 2 to 5, are not necessarily the maximum values but correspond to the equivalence ratio for which equilibrium specific impulse is the maximum. The break in the curves at about 75 weight percent fluorine in the oxidant is due to the formation of graphite.

Effect of thermodynamic data on performance. - Calculations in reference 14 show that if the carbon vapor evaporating from a graphite surface is assumed to contain the three species, monatomic carbon C, diatomic carbon C_2, and triatomic carbon C_3, then C_2 and C_3 comprise a considerable part of the vapor. In order to determine the effect on specific impulse if C_2 and C_3 were included as combustion products, additional calculations were made for 74.80 weight percent fluorine in the oxidant. This percent fluorine is near the point for maximum specific impulse and contains the largest mole fraction of C (table IV). The effect on specific impulse was small as may be seen from the following table:

Specific impulse, I, lb-sec/lb	C_2 and C_3 not included in combustion products	C_2 and C_3 included in combustion products	Decrease, percent
Equilibrium	294.0	293.1	0.31
Frozen	272.4	271.1	.48

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The effect on specific impulse should be less than shown in the preceding table for oxidants containing less fluorine.

The thermodynamic functions for C_2 and C_3 were obtained by the rigid-rotator-harmonic-oscillator approximation using the spectroscopic data of reference 15 for C_2 and the spectroscopic data suggested in reference 14 for C_3. The heats of formation for C_2 and C_3 were taken from reference 14.

3473

According to reference 7, the thermodynamic functions for CF_2, CF_3, and C_2F_2 must be regarded as tentative. However, inasmuch as the mole fractions of these substances are small (table IV), even large changes in their thermodynamic functions are expected to have only a small effect on performance.

The "low" value for the heat of dissociation of F_2, 35.6 kilocalories per mole, and the "high" value for the heat of sublimation of graphite, 171.698 kilocalories per mole at 298.16° K, which were chosen for the calculations in this report, are still open to question. The low value for F_2 tends to keep the theoretical performance low, whereas the high value for graphite tends to keep it high.

SUMMARY OF RESULTS

A theoretical investigation of the performance of JP-4 fuel with liquid fluorine - liquid oxygen mixtures for a combustion pressure of 300 pounds per square inch absolute and isentropic expansion to 1 atmosphere, assuming equilibrium and frozen composition during the expansion process, gave the following results:

1. The maximum value of specific impulse was obtained at 69.75 weight percent fluorine in the oxidant and 20.90 weight percent fuel in the propellant. The oxidant mixture is the one for which the fluorine-oxygen atom ratio equals the hydrogen-carbon atom ratio. For this oxidant mixture, the weight percent fuel in the propellant of 20.90 is the one for which the number of H atoms equals the number of F atoms and the number of C atoms equals the number of O atoms. These atom ratios may be represented by the following equivalent formula $CH_{1.942} + OF_{1.942}$.

2. The maximum value of specific impulse assuming equilibrium composition was 299.4 pound-seconds per pound. This is a 14.8 percent increase over the maximum value of 260.7 pound-seconds per pound for JP-4 fuel with liquid oxygen and a 7.4 percent increase over the maximum value of 278.9 pound-seconds per pound for JP-4 fuel with liquid fluorine.

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3. The maximum value of specific impulse assuming frozen composition was 278.9 pound-seconds per pound. This is an 11.4 percent increase over the maximum value of 250.4 pound-seconds per pound for JP-4 fuel with liquid oxygen and a 5.4 percent increase over the maximum value of 264.6 pound-seconds per pound for JP-4 fuel with liquid fluorine.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, August 11, 1954 3473

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3473

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3473

TABLE I. - PROPERTIES OF LIQUID OXIDANTS

Properties	Oxygen, O_2	Fluorine, F_2
Molecular weight, M	32.00	38.00
Density, g/cc	[a]1.1415 (at -182.0° C)	[b]1.54 (at -196° C)
Freezing point, °C	[c]-218.76	[c]-217.96
Boiling point, °C	[c]-182.97	[c]-187.92
Enthalpy required to convert liquid at boiling point to gas at 25° C	[d]3.080	[d]3.030
Enthalpy of vaporization, kcal/mole	[c]1.630 (at -182.97° C)	[c]1.51 (at -187.92° C)
Enthalpy of fusion, kcal/mole	[c].106 (at -218.76° C)	[c].372 (at -217.96° C)

[a]Ref. 12.
[b]Ref. 13.
[c]Ref. 10.
[d]Ref. 4.

TABLE II. - THEORETICAL SPECIFIC IMPULSE FOR JP-4 FUEL WITH LIQUID FLUORINE - LIQUID OXYGEN MIXTURES

[Combustion-chamber pressure, 300 lb/sq in. abs; exit pressure, 1 atm.]

Fluorine-to-oxygen atom ratio, β	Weight percent fluorine in oxidant	Equivalence ratio, r	Weight percent fuel in propellant	Specific impulse, I, lb-sec/lb	
				Equilibrium composition	Frozen composition
0	0	1.30	27.64	259.3	246.5
		[a]1.51	30.70	260.7	250.0
		1.60	31.98	259.6	250.4
0.2	19.19	1.50	28.15	269.4	255.9
		[a]1.51	28.26	269.4	256.0
		1.54	28.68	269.3	256.3
0.5	37.25	1.50	25.69	278.3	262.4
		[a]1.51	25.79	278.4	262.5
		1.60	26.94	278.2	263.4
1.0	54.29	[a]1.51	23.30	288.4	270.6
		1.55	23.80	288.5	271.1
		1.60	24.38	288.4	271.7
1.6	65.52	[a]1.51	21.57	296.6	276.9
		1.60	22.59	297.1	278.8
		1.70	23.67	294.2	277.0
1.942	69.75	1.50	20.81	299.2	278.7
		[a]1.51	20.90	299.4	278.9
		1.52	21.03	299.0	278.6
2.0	70.37	1.40	19.60	296.0	275.8
		1.48	20.49	298.9	278.4
		[b]1.53	21.04	298.1	277.7
2.1	71.38	1.40	19.44	295.7	276.1
		1.50	20.55	297.5	277.1
		[b]1.57	21.28	296.8	276.2
2.2	72.32	1.45	19.85	296.4	276.5
		1.50	20.40	296.4	276.1
		[b]1.60	21.46	295.8	275.0
2.5	74.80	1.65	21.56	293.9	272.3
		[b]1.70	22.07	294.0	272.4
		1.75	22.57	293.9	272.8
4.0	82.61	2.00	23.47	289.1	270.0
		[b]2.04	23.82	289.2	270.3
		2.20	25.22	288.7	271.2
∞	100	3.00	27.07	278.6	264.2
		[b]3.06	27.46	278.9	264.6
		3.50	30.22	278.0	266.0

[a]See eq. (7).
[b]See eq. (8).

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3473

TABLE III. - CALCULATED PERFORMANCE OF JP-4 FUEL WITH LIQUID FLUORINE - LIQUID OXYGEN MIXTURES

[Combustion-chamber pressure, 300 lb/sq in. abs; exit pressure, 1 atm; equilibrium and frozen composition assumed during expansion.]

Weight percent fluorine in oxidant	Weight percent fuel in propellant	Equivalence ratio, r	Specific impulse, I, $\frac{\text{lb-sec}}{\text{lb}}$	Characteristic velocity, c^*, ft/sec	Coefficient of thrust, C_F	Combustion chamber temperature, T_c, °K	Nozzle exit temperature, T_e, °K	Ratio of nozzle-exit area to throat area, A_e/A_t	Mean molecular weight in combustion chamber, M_c	Mean molecular weight at nozzle exit, M_e
(a) Equilibrium composition.										
00.00	30.70	1.51	260.7	5887	1.425	3428	2412	3.885	21.83	22.97
19.19	28.26	1.51	269.4	6076	1.427	3584	2570	3.913	21.37	22.78
37.25	25.79	1.51	278.4	6278	1.427	3767	2721	3.919	20.95	22.56
54.29	23.80	1.55	288.5	6523	1.423	4010	2826	3.852	20.50	22.13
65.52	22.59	1.60	297.1	6739	1.418	4255	2893	3.759	20.35	21.83
69.75	20.90	1.[illegible]1	299.4	6768	1.423	4351	3080	3.858	20.71	22.37
70.37	20.49	1.48	298.9	6759	1.423	4359	3077	3.849	20.80	22.47
71.38	20.55	1.50	297.5	6723	1.424	4332	3076	3.865	20.91	22.59
72.32	20.40	1.50	296.4	6697	1.424	4321	3064	3.862	21.04	22.70
74.80	22.07	1.70	294.0	6617	1.429	4204	3118	3.984	21.42	22.85
82.61	23.82	2.04	289.2	6495	1.433	4184	3155	4.040	22.21	23.61
100.00	27.46	3.06	278.9	6240	1.438	4146	3219	4.140	24.03	25.37
(b) Frozen composition.										
00.00	30.70	1.51	250.0	5733	1.403	3428	1929	3.500	21.83	
19.19	28.26	1.51	256.0	5890	1.398	3584	1935	3.410	21.37	
37.25	25.79	1.51	262.5	6061	1.394	3767	1945	3.314	20.95	
54.29	23.80	1.55	271.1	6280	1.389	4010	1978	3.219	20.50	
65.52	22.59	1.60	278.8	6468	1.387	4255	2048	3.170	20.35	
69.75	20.90	1.51	278.9	6474	1.386	4351	2075	3.152	20.71	
70.37	20.49	1.48	278.4	6464	1.386	4359	2075	3.147	20.80	
71.38	20.55	1.50	277.1	6432	1.386	4332	2072	3.157	20.91	
72.32	20.40	1.50	276.1	6407	1.386	4321	2074	3.164	21.04	
74.80	22.07	1.70	272.4	6304	1.390	4204	2105	3.249	21.42	
82.61	23.82	2.04	270.3	6228	1.396	4184	2218	3.369	22.21	
100.00	27.46	3.06	264.6	6047	1.408	4146	2435	3.597	24.03	

TABLE IV. - EQUILIBRIUM COMPOSITION IN COMBUSTION CHAMBER FOR JP-4 FUEL WITH LIQUID FLUORINE - LIQUID OXYGEN MIXTURES

[Combustion-chamber pressure, 300 lb/sq in. abs]

Weight percent fluorine in oxidant	0	19.12	37.95	54.29	65.52	69.75	70.37	71.36	72.32	74.80	82.61	100.00
Weight percent fuel in propellant	30.70	28.26	25.79	25.60	22.59	20.90	20.42	20.56	20.40	22.07	25.82	27.46
Equivalence ratio, r	1.508	1.508	1.508	1.550	1.600	1.508	1.480	1.500	1.800	1.700	2.040	3.080
Equilibrium composition (mole fraction)												
C	0.00000	0.00000	0.00000	0.00000	0.00000	0.00019	0.00004	0.00282	0.00375	0.00784	0.00638	0.00428
Graphite	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.01138	.11272	.28354
CF	.00000	.00000	.00000	.00000	.00000	.00017	.00004	.00287	.00403	.00698	.00625	.00504
CF_2	.00000	.00000	.00000	.00000	.00000	.00001	.00000	.00010	.00015	.00021	.00021	.00020
CF_3	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00001	.00002	.00002	.00002	.00002
C_2F_2	.00000	.00000	.00000	.00000	.00000	.00001	.00000	.00230	.00475	.02414	.02366	.02269
CO	.37285	.35502	.33841	.33045	.32741	.30940	.30486	.29721	.28979	.25989	.16314	.00000
CO_2	.10707	.07740	.04840	.01277	.00162	.00003	.00017	.00000	.00000	.00000	.00000	.00000
F	.00020	.00138	.00563	.02023	.05696	.10288	.11393	.10948	.11205	.06210	.05716	.04861
H	.03959	.05110	.06431	.08022	.09040	.07428	.06910	.06606	.06259	.07322	.06694	.05609
H_2	.12903	.10623	.07921	.05031	.02876	.01453	.01230	.01217	.01127	.02235	.02218	.02176
HF	.00000	.15352	.29921	.42602	.46614	.49834	.49852	.50702	.51159	.53187	.54133	.55775
H_2O	.29805	.19029	.09500	.02447	.00124	.00001	.00006	.00000	.00000	.00000	.00000	.00000
O	.00802	.01359	.02094	.02287	.00490	.00015	.00077	.00001	.00001	.00000	.00000	.00000
O_2	.00709	.00932	.00961	.00426	.00008	.00000	.00000	.00000	.00000	.00000	.00000	.00000
OH	.03829	.04216	.03930	.02240	.00248	.00005	.00022	.00000	.00000	.00000	.00000	.00000

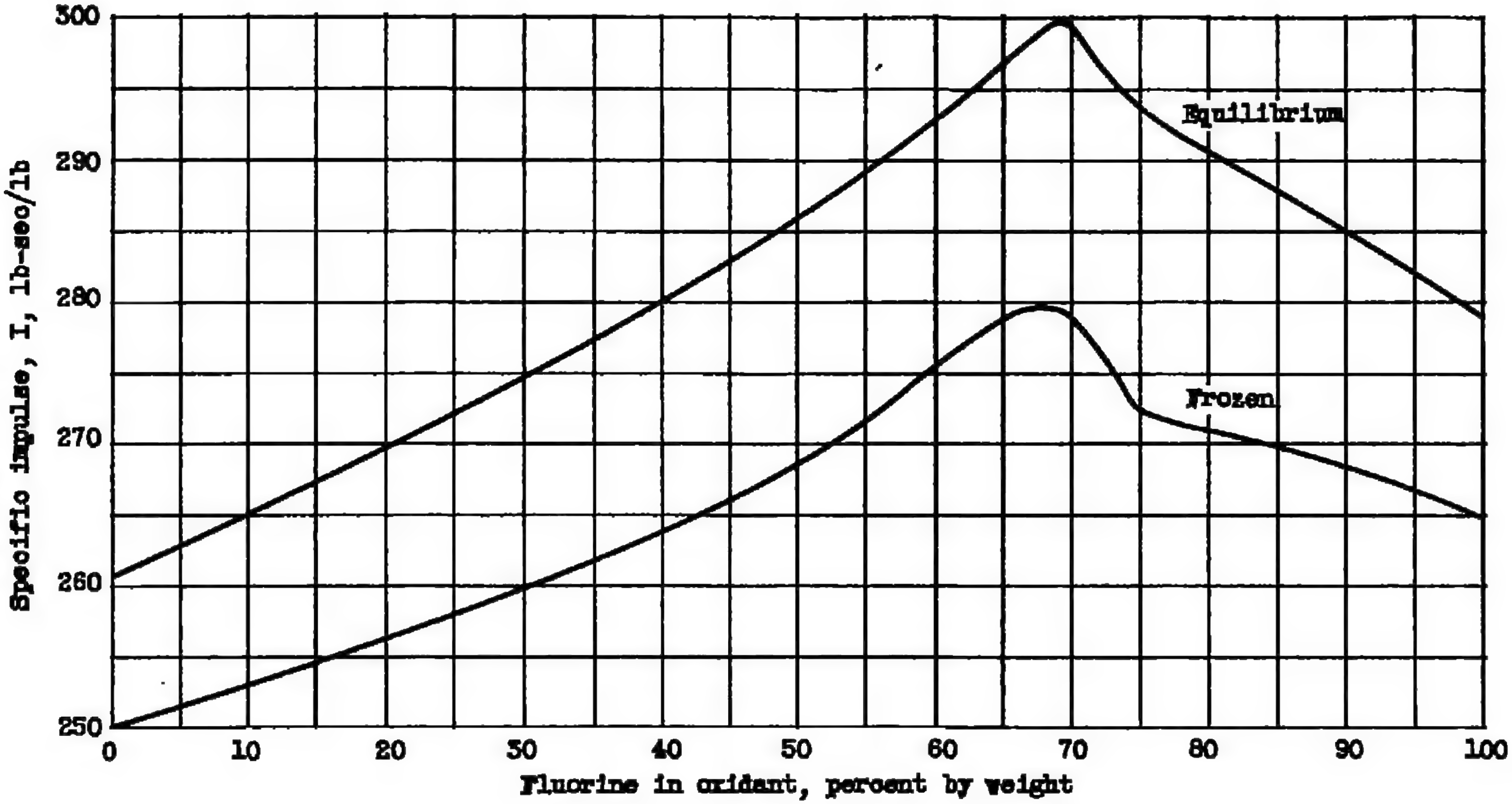

Figure 1. - Theoretical specific impulse of JP-4 fuel with liquid fluorine - liquid oxygen mixtures at equivalence ratios for which equilibrium specific impulse is maximum. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere assuming equilibrium and frozen composition.

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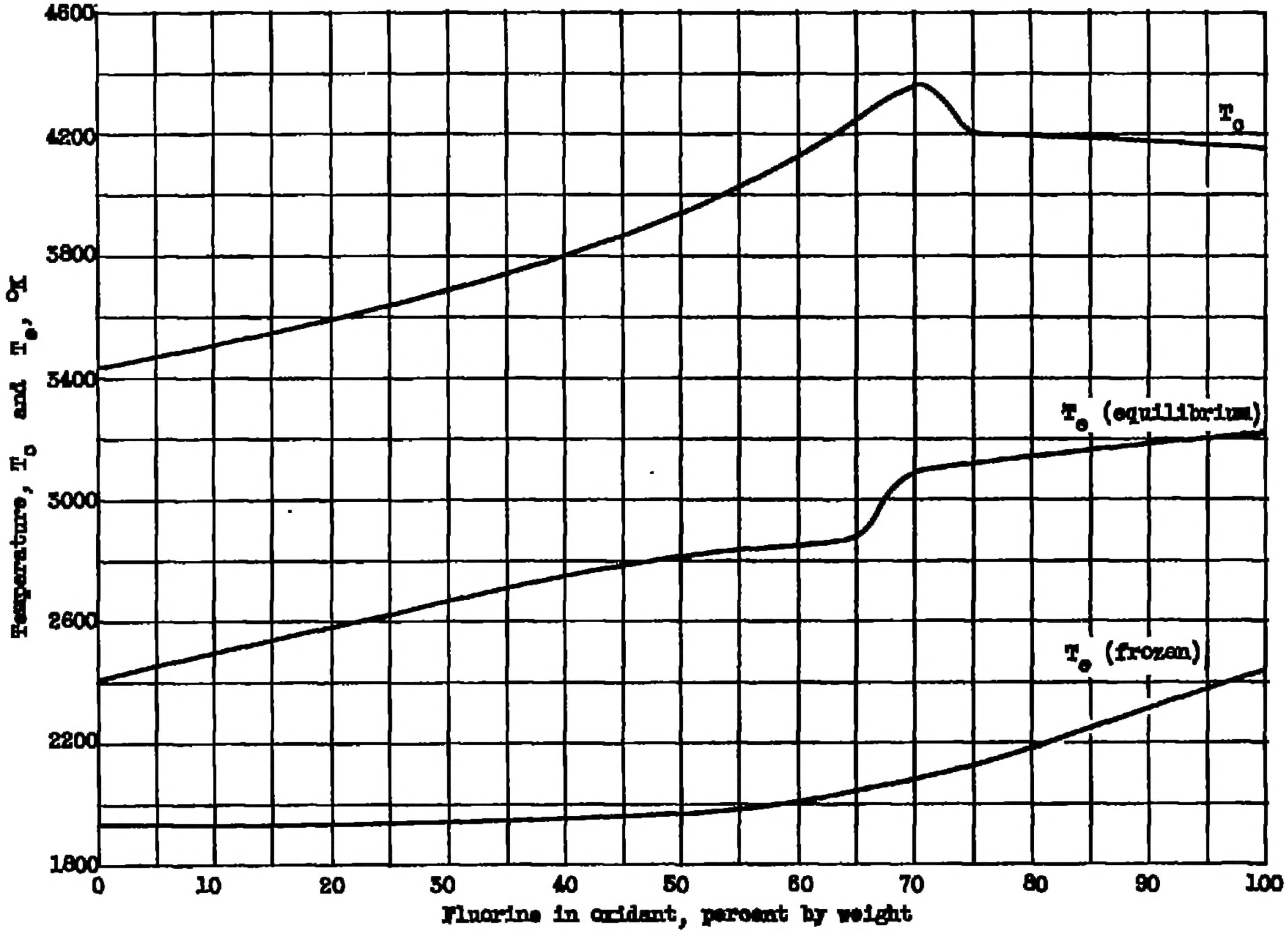

Figure 2. - Theoretical combustion-chamber temperature and nozzle-exit temperature of JP-4 fuel with liquid fluorine - liquid oxygen mixtures at equivalence ratios for which equilibrium specific impulse is maximum. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere assuming equilibrium and frozen composition.

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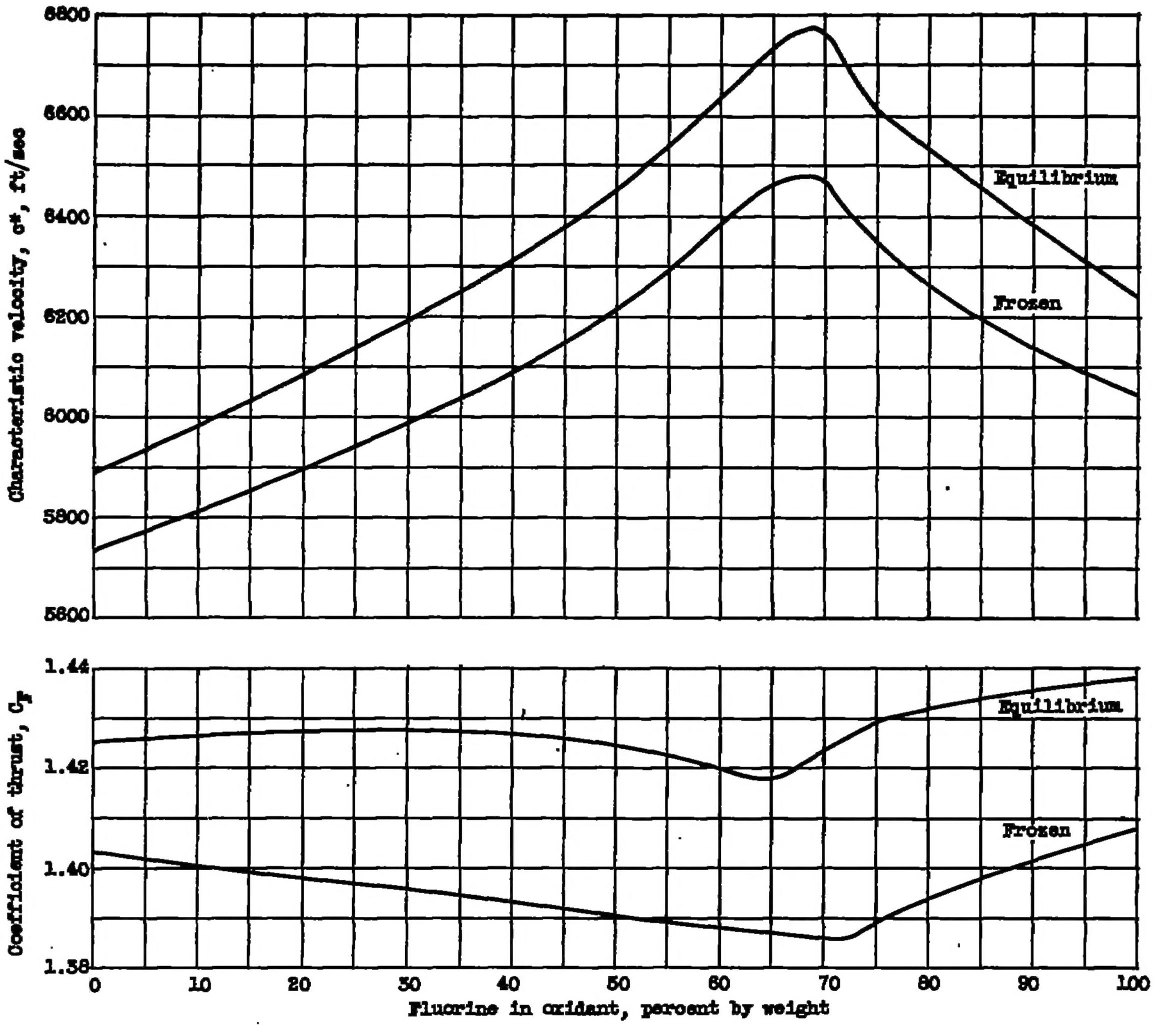

Figure 3. - Theoretical characteristic velocity and coefficient of thrust of JP-4 fuel with liquid fluorine - liquid oxygen mixtures at equivalence ratios for which equilibrium specific impulse is maximum. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere assuming equilibrium and frozen composition.

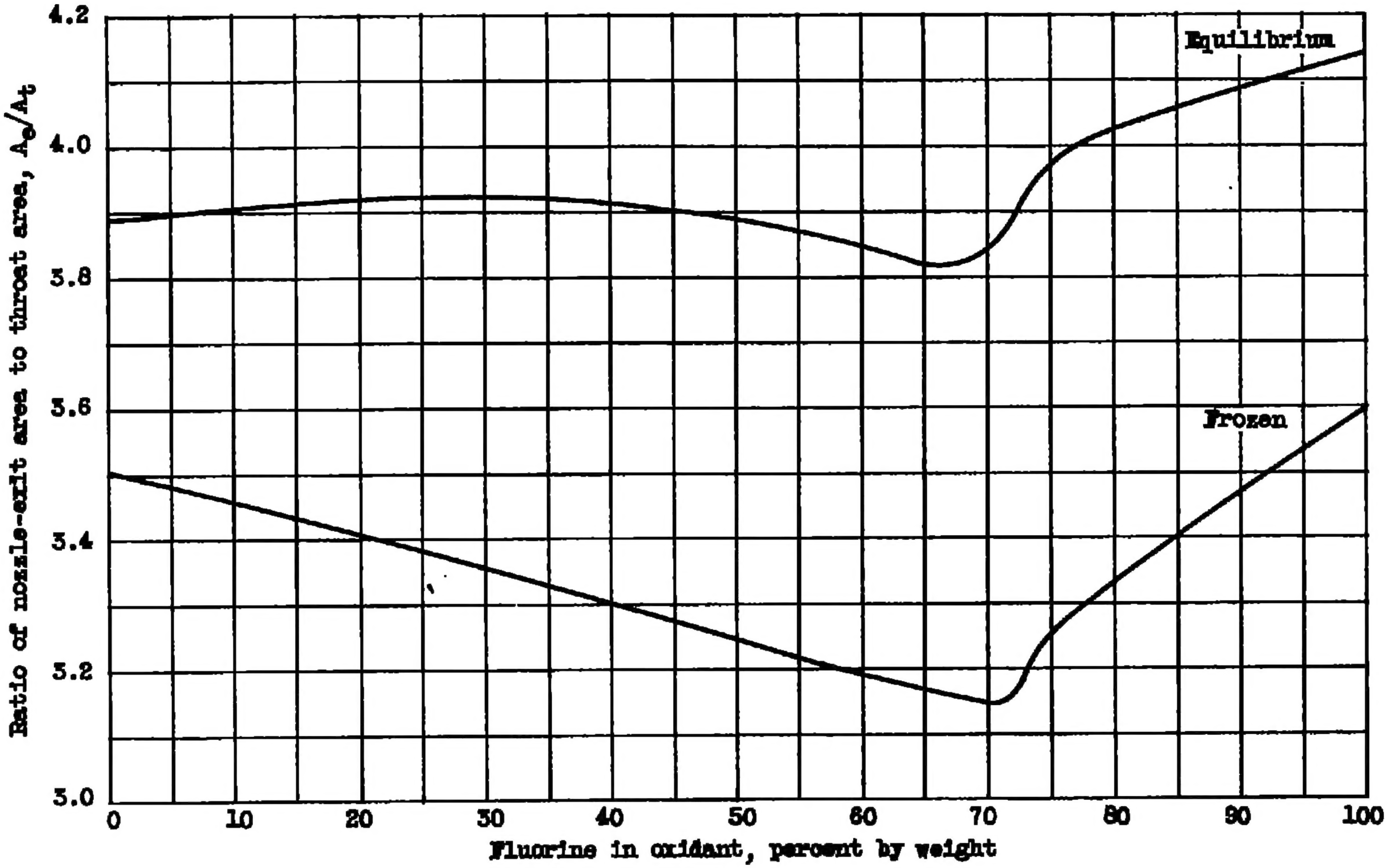

Figure 4. - Theoretical ratio of nozzle-exit area to throat area of JP-4 fuel with liquid fluorine - liquid oxygen mixtures at equivalence ratios for which equilibrium specific impulse is maximum. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere assuming equilibrium and frozen composition.

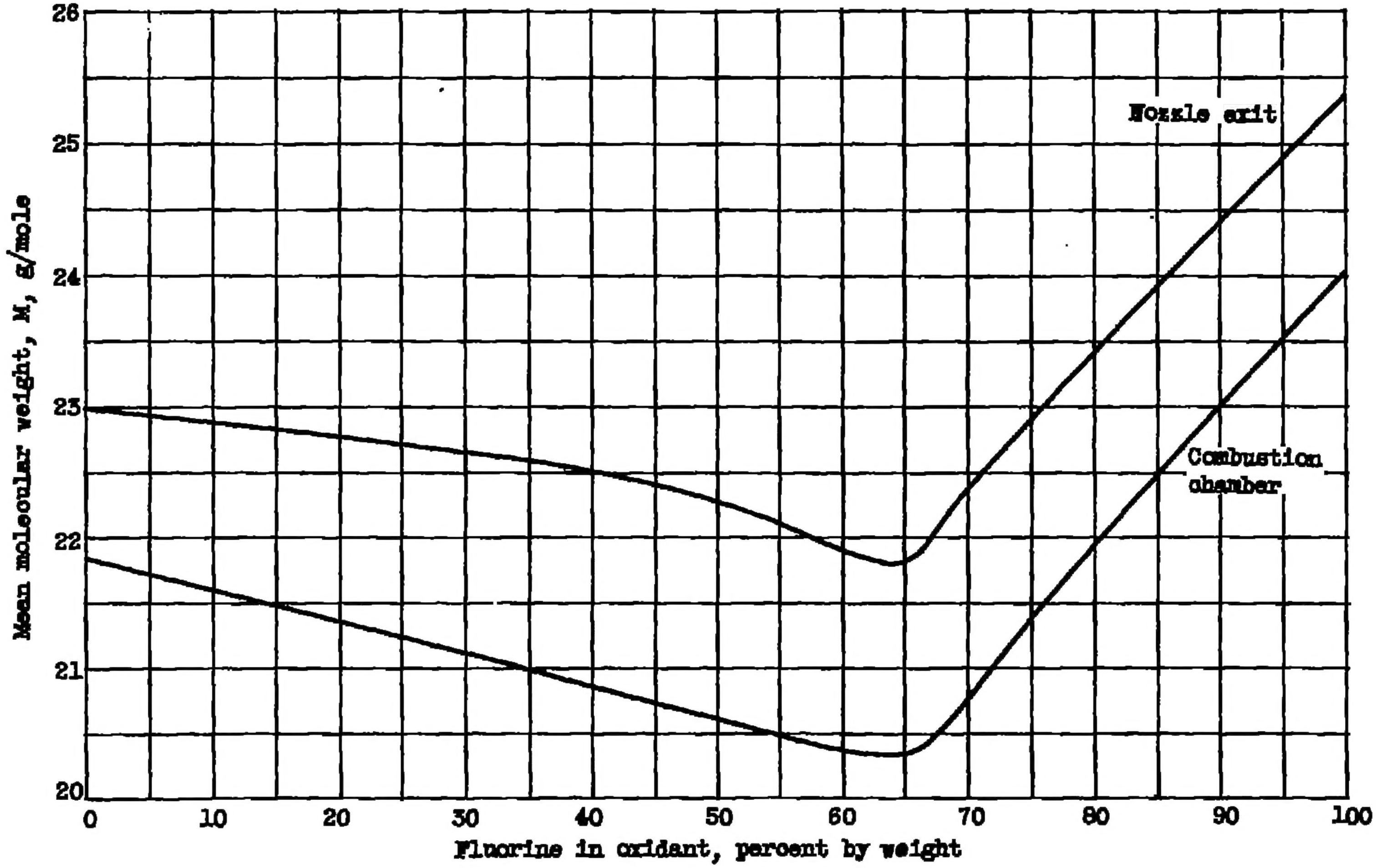

Figure 5. - Theoretical mean molecular weight in combustion chamber and at nozzle exit of JP-4 fuel with liquid fluorine - liquid oxygen mixtures at equivalence ratios for which equilibrium specific impulse is maximum. Isentropic expansion from 300 pounds per square inch absolute to 1 atmosphere assuming equilibrium composition.